PRISTINE SIC CANDIDATES: SPECTRAL IMAGING AND AUGER ANALYSIS. T. K. Croat, E. Lebsack

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Introduction: A significant fraction of pristine SiCs (e.g. those located without the aid of acid dissolution) show an amorphous surface coating that is not present on acid-treated SiCs or on other grains from the meteorite residue [1]. Since these grains traversed the interstellar medium and early solar system as solid objects, these coatings could be a preserved feature of those environments. One of two coated grains measured for N isotopes in the NanoSIMS showed indications of a ^{15}N-rich coating on a SiC grain with a bulk ^{14}N enrichment [2], and such ^{15}N enrichments could conceivably result from low temperature interstellar chemistry [3]. However, due to the limited material that comprises the SiC surface, studies of the isotopic composition of SiC surface layers will likely have to be statistical in nature, such as comparison of populations of coated SiCs vs. uncoated ones, and many more pristine SiCs will be required. In this work, we describe a new spectral imaging method to quickly find more such pristine SiCs and present images and Auger electron spectra from these grains.

Experimental: About 30mg of material was excavated from the Murchison matrix, ultrasonicated in an isopropanol-water mixture for several hours, and then pipetted onto graphite planchets. Pristine SiCs (with ~15 ppm abundance in Murchison [4]) were located using spectral imaging with a Noran System 6 energy dispersive x-ray spectrometer (EDXS) on a JEOL JSM840a SEM. Although procedures were analogous to [1], Si count rates were optimized (at the expense of image and spectral resolution) through higher beam currents (~$1x10^{-8}$ A) and a faster EDXS time constant, and a higher magnification (600x) was used to increase the detection efficiency of smaller (<0.5 μm) SiCs. Although principal component analysis and other advanced techniques were attempted to locate SiCs in the spectral image datasets (which produce a full spectrum at each pixel), the simpler method of overlaying Si counts in red and Mg counts in green made SiCs clearly stand out visually from silicates and other Si-rich phases (see Fig 1). SiCs can be distinguished from silicates by their lower Mg and O content. EDXS spectra were then collected from SiC candidates at higher magnifications to improve the compositional data. High-resolution images and Auger spectra were taken with a PHI 700 Scanning Auger Nanoprobe (30-2300 eV energy range) to confirm the grains as SiC.

Results and Discussion:
Figure 2 shows the Mg/Si and O/Si ratios from the Si-rich and relatively Mg-poor subset of grains in the
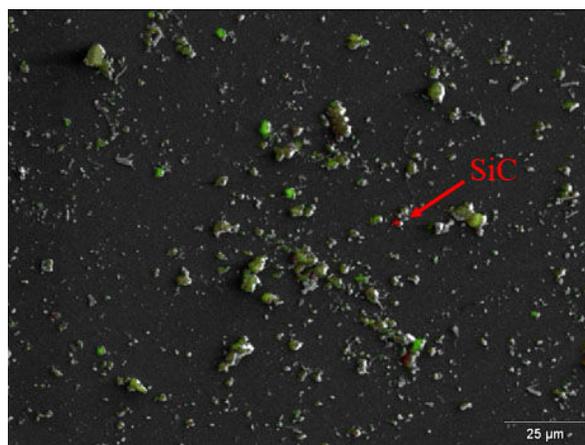

Fig. 1. Secondary electron image overlaid with x-ray maps (Si in red, Mg in green) with bright red SiC clearly visible (same SiC is shown in Fig 2a image).
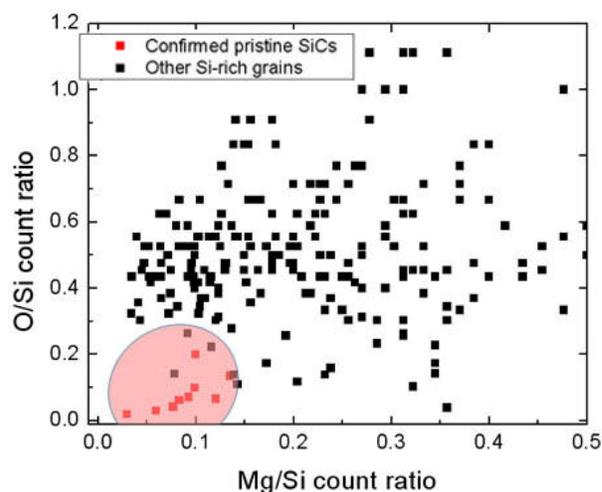

Fig. 2. Mg/Si and O/Si x-ray count ratios from confirmed SiCs and other Si-rich grains. The range in which pristine SiCs are found is outlined.

Murchison residue (defined by >50 Si counts and <25 Mg counts, and which constitute ~0.2% of total grains). Grains confirmed as SiC (via high resolution images and EDXS spectra) are compositionally distinct from the other Si-rich grains. There are a small number of non-SiC grains at upper edge of the outlined SiC region in Fig. 2, but fortunately these have a lower abundance than SiC and also can be easily distinguished in high-resolution images by their porous appearance. The SiC abundance is estimated at ~30 ppm, roughly in agreement with [4]), but with considerable uncertainty because of the highly variable grain density on the graphite planchet. When

measured again by EDXS at higher magnifications and with longer acquisition times, the Mg and O content of pristine SiCs are ~4x and ~2x lower, respectively, than in spectral images (which would effectively compress both ratios in Fig. 1). EDXS measurements were also made on Murchison KJG SiCs prepared by conventional acid dissolution, and these showed considerably lower Mg and O content than the pristine SiCs (measured under identical conditions). The average Mg/Si and O/Si count ratios were 0.02 and 0.05 for pristine SiCs, as opposed to 0.001 and 0.007 in the KJG SiCs. Figure 3 shows higher magnification secondary electron images of two pristine SiCs found using spectral imaging. The smaller SiC (Fig 3b) shows a more prominent coating, and with a geometrical mean size of ~0.8 mm, demonstrates that the spectral imaging method can easily detect SiCs of a micron or smaller in size. The average geometric mean diameter of pristine SiCs found thus far is 1.2 μm with a range from 0.8-1.9 μm.

Auger electron spectra of pristine SiCs showed C, O and sometimes Si, Mg and trace amounts of N and Fe. In some cases, Si peaks were not seen in differentiated AES spectra from pristine SiCs, indicating that grain coatings are not Si-rich and that they can exceed the thickness from which Auger electrons are generated (a few nm). Coated pristine SiCs show a slightly stronger C signal than uncoated ones and both of these groups have far stronger C content than the bare surfaces of chemically-etched KJG SiCs. These results show that the SiC coatings are mainly carbonaceous. Because of the atmospheric O contamination present on all sample surfaces, it is difficult to assess whether or not the SiC coatings also contain O. No significant difference is seen between the O signal strength of AES spectra from coated or uncoated pristine SiCs or from chemically-etched KJG SiCs. NanoSIMS O depth profiles of pristine SiCs will be taken to give more insight into the O content of the coatings.

Although Auger quantitative analysis of Mg/Si ratios is not possible due to weak signals and considerable uncertainty in sensitivity factors, Auger spectra suggest that the Mg content of the pristine SiC surfaces is higher than the bulk. Coated pristine SiCs show slightly higher Mg content in AES than uncoated ones and both are considerably higher than chemically-etched KJG SiCs. Thus, some of the higher Mg content from pristine SiC seen in EDXS is correlated with the grain surface. However, the ability of a thin surface layer to alter the SiC bulk composition in EDXS is limited. Thus, the higher Mg content of the pristine SiCs may also reflect inherent differences in bulk Mg content between the smaller pristine grains and the larger KJG SiCs (with ~3 μm average size). Further, it will be interesting to see if any of the Mg-

rich pristine SiCs are found to be SiC-X grains (with ^{26}Mg excesses from decayed ^{26}Al) during upcoming isotopic studies.
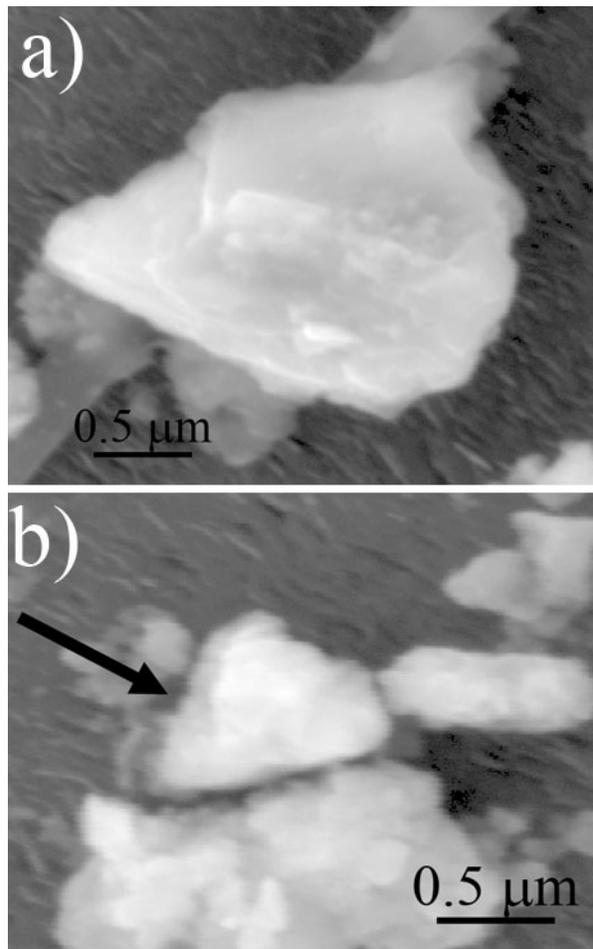

Fig. 3. Secondary electron images of two pristine SiCs located with spectral imaging technique.

References: [1] Bernatowicz T.J. et al. (2003) *GCA 472*, 760. [2] Croat T.K. et al. (2009) *LPS XL*, Abstract # 1887. [3] Floss et al. (2004) *Science*, 303, 1355. [4] Huss, G.R. (1997), in *Astrophysical Implications of the Laboratory Study of Presolar Materials*, eds. T. J. Bernatowicz, & E. Zinner (New York: AIP), 721.