

AUGER AND NANOSIMS INVESTIGATIONS OF PRISTINE PRESOLAR SiC SURFACES. T. K. Croat, T.J. Bernatowicz, and F. J. Stadermann, Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130, USA, tkc@wustl.edu.

Introduction: A significant fraction of pristine SiCs (those prepared without harsh acid treatments) showed an apparently amorphous surface coating not seen on other grains in the Murchison residue (e.g. Fig. 7 from [1]) or on conventionally-prepared presolar SiCs. Since presolar SiCs are known to have traversed various astrophysical environments (e.g. ISM, early solar system), these coatings could be a preserved feature of these environments. Here, we report preliminary results from an investigation of 15 pristine SiC surfaces with Auger Electron Spectroscopy and subsequent NanoSIMS measurement of 3 SiCs.

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 were then located on these planchets using automated X-ray mapping of the Si, Mg and O lines (for details see [1]). High-resolution (HRSEM) images of SiCs were taken with a Hitachi S-4500 field emission SEM and Auger spectra were acquired with a PHI 700 Scanning Auger Nanoprobe (30-2300eV energy range). NanoSIMS isotopic measurements of ^{12}C , ^{13}C , ^{16}O , $^{12}\text{C}^{14}\text{N}$, and $^{12}\text{C}^{15}\text{N}$ were collected as a function of depth. The sample was not pre-sputtered, so standards were used to correct the data for preferential sputtering effects in early layers. However, this ~10% correction was only required for $^{12}\text{C}/^{13}\text{C}$ and did not materially change the observed ratios.

Results and Discussion: The surface-sensitive Auger spectra of pristine SiCs showed C, O and sometimes Si and trace amounts of N, Mg or Fe. The absence of Si peaks in some SiCs indicates that the amorphous coating thickness can exceed the depth from which Auger electrons are generated (a few nm), and this situation was more common in spectra from coated SiCs (7 of 12 spectra) than in those from uncoated SiCs (1 of 12). The Si relative intensity from coated SiCs was also lower than from surrounding grains (mostly silicates), suggesting that this coating was a characteristic of the pristine SiCs but not of all grains in the residue. The relative strength of the Si signal increased considerably after the surface was sputtered by NanoSIMS experiments. Overall, these findings confirm that the coatings first observed in HRSEM are indeed present, and consist mainly of C (and perhaps O) without a strong Si component.

Figure 1 (a-c) shows the C and N isotopic ratios as a function of layer (sputtering depth) in N-rich sub-regions from 3 SiC surfaces (2 coated and 1 uncoated). The h2-97 coated SiC (Fig. 1a) appears to show an isotopic transition in $^{14}\text{N}/^{15}\text{N}$ and $^{12}\text{C}/^{13}\text{C}$ near layer 5,

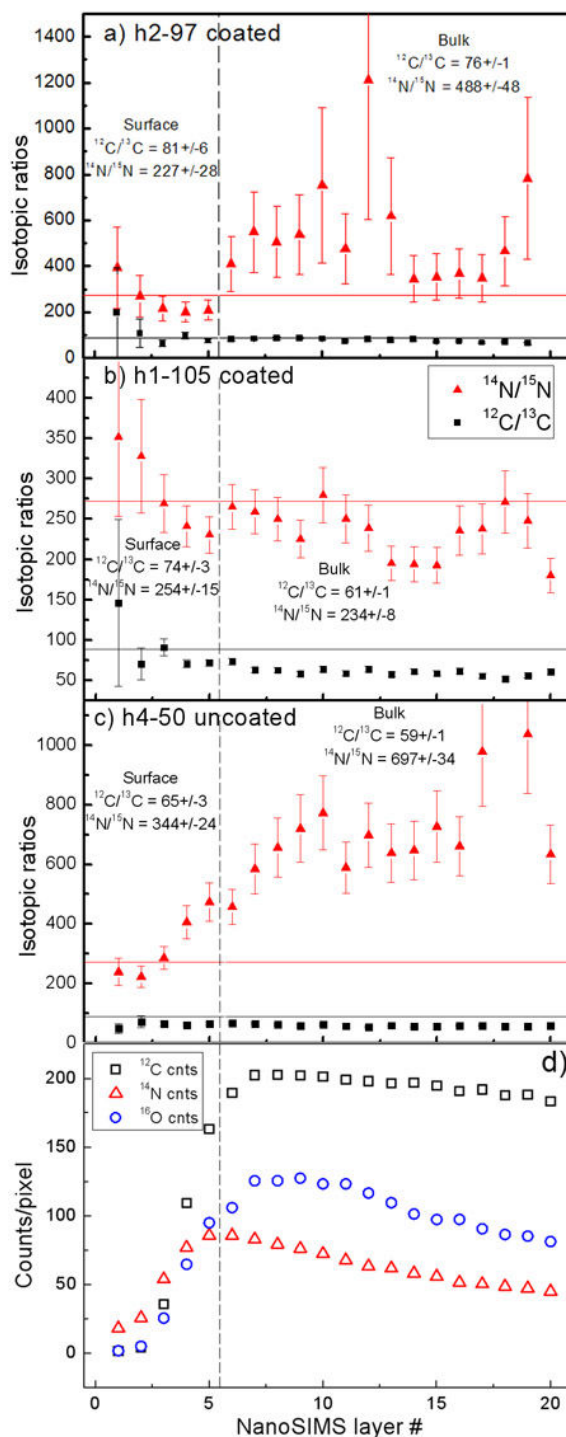


Fig. 1. $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$ ratios vs. NanoSIMS measurement layer from N-rich sub-regions of: a) h2-97 coated SiC b) h1-105 coated SiC and c) h4-50 uncoated SiC; d) typical ^{12}C , ^{14}N and ^{16}O count rates per pixel (from h1-105)

so on this basis its “surface” is defined as layers 1-5. From the time required to sputter away other grains during the experiment, this surface is estimated to be ~20 nm thick. The counts in Fig. 1a are integrated over a slightly N-rich sub-region comprising ~25% of the entire SiC surface. The data suggest that the surface is ^{15}N -rich (significant at 1.6σ level) whereas the SiC bulk (layers 6-20) is ^{14}N -rich (a typical anomaly for mainstream SiCs). Other N-poorer regions of h2-97 show solar N at the surface (within errors) but again a ^{14}N -rich bulk. ^{15}N -enrichments, such as that suggested by the surface above, are often associated with interstellar molecular clouds [2]. Such a ^{15}N -rich surface could be produced by irradiation of ices deposited on the SiCs during their residence in dense molecular clouds [3]. Fig. 1b from the surface of the h1-105 coated SiC shows a solar N composition at the surface with a ^{15}N enriched bulk. Although their surfaces appear shallower (~3 layers or less) in terms of the transitions in C and N ratios, for consistency the same criterion for the surface (layers 1-5) is used for the other SiCs (h1-105 coated and h4-50 uncoated). Despite its low $^{14}\text{N}/^{15}\text{N}$ bulk composition, h1-105 is most likely still a mainstream SiC and among the 10% of such grains with subsolar N ratios. However, since the bulk nucleosynthetic anomaly shows ^{15}N enrichment, on such a grain it would never be possible to attribute any ^{15}N enrichments to secondary processes acting on the SiC surfaces. The uncoated SiC (h4-50 in Fig. 1c) is a typical mainstream SiC whose early measurement layers (“surface”) show a similar C ratio to its bulk. Although its N surface ratios are diluted toward solar, it does not show any C isotopic distinctions between surface and bulk, as might be expected for a SiC which did not appear to be coated in HRSEM. The area over which C and N counts were integrated excludes a significant fraction of the SiC surface that showed a solar-like isotopic composition in $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$ throughout all 20 measurement layers. Fig. 2 shows a $^{12}\text{C}/^{13}\text{C}$ isotopic ratio image wherein this 400 by 500 nm area (blue region indicated by arrow), despite otherwise looking like part of the SiC, has a roughly solar C isotopic composition. Although we lack information on ^{16}O due to a detector failure, post-SIMS Auger spectra show stronger Mg and O and weaker Si from the solar region. Fig. 1d shows the typical count rates per pixel for ^{12}C , $^{12}\text{C}^{14}\text{N}$ and ^{16}O . The CN^- count rates per pixel rose immediately to ~1/2 of their maximums (Fig. 1d), allowing more accurate N isotopic surface measurements of the surfaces, whereas C^- and O^- count rates rose much more slowly (~1% of max in first layer).

Prominent N hotspots (~250 nm in size) were seen in the uncoated SiC (h4-50) and in one of the uncoated

SiCs (e.g. h1-105 in Fig. 3). These N hotspots have ~4x higher CN^-/C^- ratios than surrounding regions, and the N-richness persisted through all layers. This suggests that the N hotspots are a property of the bulk mainstream SiCs, rather than being related to their surfaces, and these might be associated with N-rich internal subgrains.

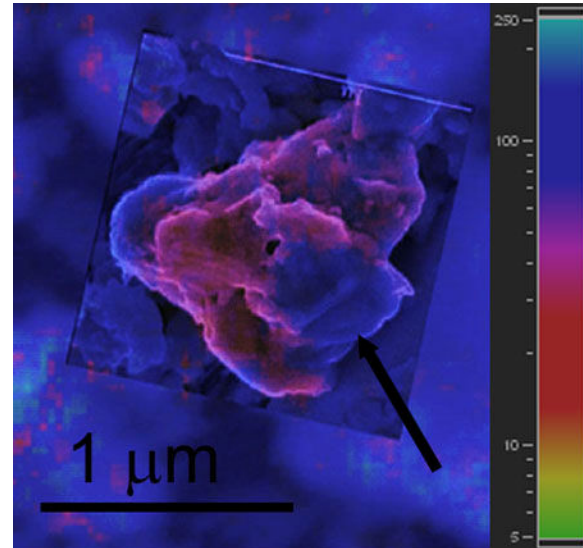


Fig. 2. $^{12}\text{C}/^{13}\text{C}$ isotopic ratio image of h4-50 uncoated SiC, showing “overgrown” region with solar C ratio.

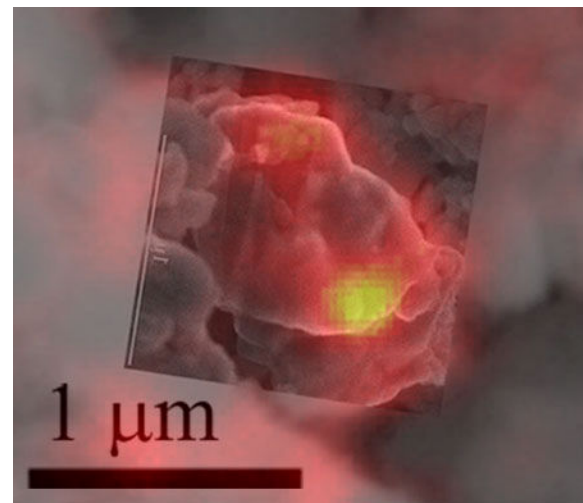


Fig. 3. High resolution SEM images of h1-105 overlaid with a colorized ^{14}N count map; bright yellow region toward bottom of SiC indicates an N hotspot.

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References: [1] Bernatowicz T.J. et al. (2003) *GCA* 472, 760. [2] Floss et al. *Science*, 303, 1355. [3] Sandford et al. (1997) *From Stardust to Planetesimals*, 201.