SURFACE AND INTERNAL STRUCTURE OF PRISTINE PRESOLAR SILICON CARBIDE. Rhonda M. Stroud[1] and Thomas J. Bernatowicz[2], [1]Naval Research Laboratory, Code 6371, 4555 Overlook Avenue NW, Washington, DC 20375 (stroud@nrl.navy.mil), [2]Laboratory for Space Sciences, Washington University, 1 Brookings Drive, St. Louis, MO 63130.

Introduction: Silicon carbide is the most well-studied type of presolar grain. Isotope measurements of thousands [1,2] and structural data from over 500 individual grains have been reported [3]. The isotope data indicate that approximately 98% originated in asymptotic giant branch stars and 2% in supernovae. Although tens of different polytypes of SiC are known to form synthetically, only two polytypes have been reported for presolar grains. Daulton et al. [3] found that for SiC grains isolated from Murchison by acid treatments, 79.4% are 3C cubic β-SiC, 2.7% are 2H hexagonal α-SiC, 17.1% are intergrowths of α and β, and 0.9% are heavily disordered. They report that the occurrence of only the α and β polytypes is consistent with the observed range of condensation temperatures of circumstellar dust for carbon stars. Further constraint on the formation and subsequent alteration of the grains can be obtained from studies of the surfaces and interior structure of grains in pristine form, i.e., prepared without acid treatments [4,5]. The acid treatments remove surface coatings, produce etch pits around defect sites and could remove some subgrains. Surface oxides have been predicted by theoretical modeling as a survival mechanism for SiC grains exposed to the hot oxidizing solar nebula [6]. Scanning electron microscopy studies of pristine SiC shows some evidence for the existence of oxide and organic coatings [4]. We report herein on transmission electron microcopy studies of the surface and internal structure of two pristine SiC grains, including definitive evidence of an oxide rim on one grain, and the presence of internal TiC and AlN grains.

Experimental: The pristine, physical separate grains were prepared by crushing and ultrasonicating a piece of Murchison, then dispersing the residue on a graphite stub, on which the grain was identified as SiC by x-ray mapping [4]. We prepared ultra-thin sections of the grains for transmission electron microscopy (TEM) using a focused ion beam workstation (FIB) lift-out technique adapted to free-standing grains [7]. The TEM studies were carried out using JEOL 2200 FS and JEOL 2010F microscopes equipped with a NORAN Vantage energy dispersive x-ray spectroscopy (EDS) system. To preserve the surface structure of the grains, no isotope measurements were made prior to the TEM analysis. Future NanoSIMS analysis of the ultra-thin sections will permit classification of the presolar origin.

Results and Discussion: Grain 23 exhibits a surface oxide rim and highly complex internal structure, as shown Figures 1 and 2. Electron diffraction from the grain indicates that is made up of multiple crystallites of the 3C cubic β-SiC polytype. Whole-grain-average EDS measurements show trace amounts of Ti, Fe and Al in addition to SiC. The Ti and Al appear to occur as distinct TiC and AlN inclusions, rather uniformly in solution. The inclusions are clearly visible with Z-contrast imaging, but difficult to detect by conventional bright-field and high-resolution imaging because TiC and AlN are isostructural to SiC, with lattice constants differing by hundredths of angstroms. The presence of an oxide rim, visible in both the conventional and Z-contrast images, is confirmed by the decrease in the C:O ratio from ~10:1 in the grain middle, to ~2:1 at the grain edges. The rim appears to be mostly silica with trace amounts of Al, Ti and Fe.

Grain 93 has a simpler morphology, with no discernable rim. The grain-average EDS measurements show SiC plus trace amounts of Ti and Al. The Z-contrast analysis (Figure 3) shows some bright inclusions, which we identified by EDS to be TiC. The dark inclusions (bottom right edge, Figure 3) contain Si, O, Fe, Mg, Ni, Cr, Ca, S, and Cl. The composition and near-edge location of this material suggest that it is a product of in-filling of surface pits in the SiC by matrix minerals, and not a circumstellar condensate. The crystal structure of the grain itself is problematic. The diffraction patterns are single-crystal-like, with no sign of twining or stacking faults. Many, but not all of the measured d-spacings are consistent with the α-SiC 2H structure, and one zone axis pattern can be indexed to the [201] 2H zone. However, two other zone axis patterns do not index to 2H, 4H, 6H, 3C or 15R polytypes. High-resolution TEM is the best method for identifying unusual polytypes of SiC, but this section is too thick to yield lattice-resolution images.

The results from grains 23 and 93 show that despite the great number of SiC grains previously studied, the interior and surface structure of non-etched grains remains a fruitful area of investigation. In particular, we have learned that interior TiC and AlN may be quite common, although they have only previously been reported for a single grain [8]. The under-representation in the literature data is likely due to the difficulty of detecting these phases in SiC by conventional imaging techniques, particualry without microtoming or FIB preparation. We also now know that silica rims do occur on some SiC grains. The diffraction data from grain 93 may indicate the occurrence of a third polytype, but further analysis is required.

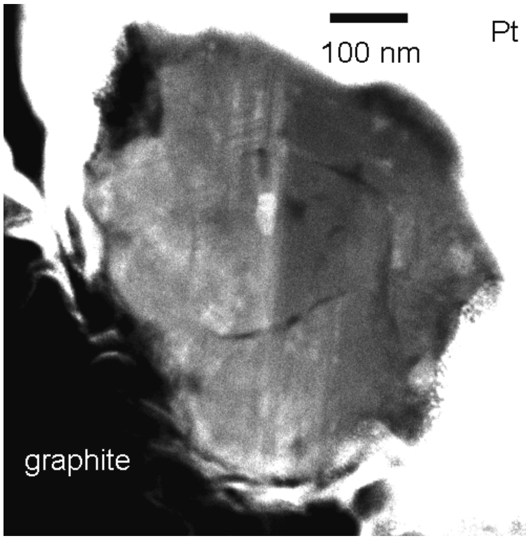

Figure 1. Z-contrast image of SiC grain 23. High atomic number areas appear bright and low atomic number areas appear dark in this image mode. The grain shows significant internal composition variation, as indicated by the bright and dark subgrains, planar striations, and a dark triangular boundary. The oxide rim is a dark band 10 to 30 nm thick around the exterior of the grain.

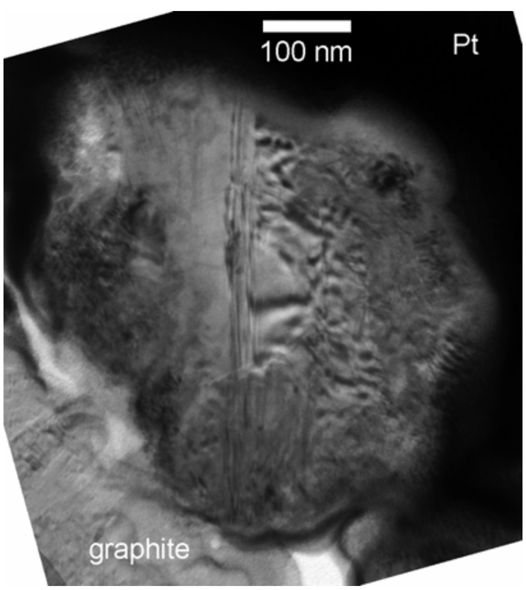

Figure 2. Conventional bright-field TEM image of SiC 23. The contrast in this image is dominated by diffraction effects. The vertical planar defects are related to the striations in Figure 1.

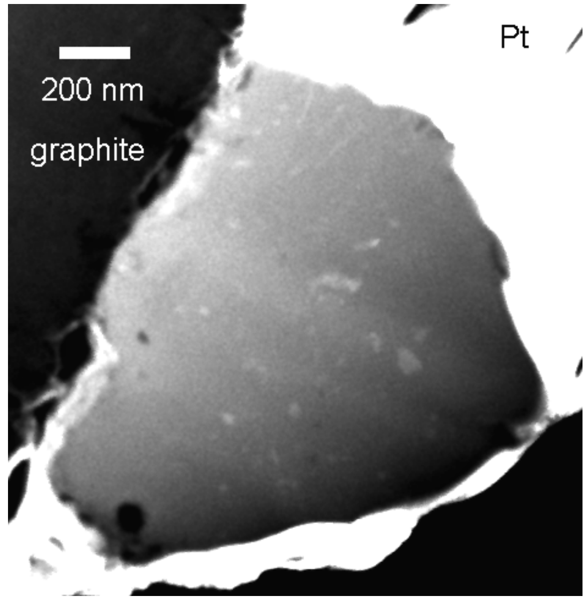

Figure 3. Z-contrast image of SiC grain 93. The grain edges are sharp, with no sign of an oxide rim. The light colored inclusions are interior TiC grains. The dark inclusions in the lower right are not true subgrains, but infill of meteorite matrix material.

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